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Charge decay characteristics of polystyrene

M S Gour[1], P K Khare* and Ranjeet Singh
[1]Department of Physics, Hindustan College of Science & Technology, Farah, Mathura, Uttar Pradesh, India
*Department of Post Graduate Studies and Research in Physics and Electronics,
Rani Durgavati University, Jabalpur-482 001, Madhya Pradesh, India

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Abstract : The charge decay behavior of polystyrene (PS) samples, ≈ 40 μm in thickness, was investigated by means of transient currents (in charging and discharging mode) and thermally stimulated discharge currents (TSDC) measurements as a function of polarizing fields, and temperatures. The order of currents has been found to increase with increasing these parameters. The current-time characteristics have different values of slopes lying between 0.45 to 0.65 and 1.66–1.99. The TSDC thermograms of PS consist of a peak located around 60–85°C. Comparative studies of the isochronal characteristics (*i.e.* current-temperature plots at constant times) with the thermally stimulated discharge current, indicated a strong resemblance between two techniques. It is suggested that both the dipolar orientation due to molecular mechanism of motions with the side chains and space charges due to trapping of injected charge carriers in energetically distributed traps may be responsible for the observed currents.

Keywords : Charge decay, transient currents, thermally stimulated discharge currents, dipolar orientation, space charge mechanism.

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The mechanism and character of conduction in polymers has been the subject of many investigations. The movement of charge carriers in polymeric dielectrics has received a great attention because of its importance in science and technology [1,2]. The thermally stimulated discharge current (TSDC) technique is a simple but effective tool for extracting information about the internal structure and molecular relaxations, as well as the establishment and decay of space charge due to trapping of charge carriers and their subsequent thermal release from traps in polymers [3,4]. TSDC reveals the molecular mobility of the material's structure as well as the movement of the charge accumulated at different interfaces [5]. Transient currents observed upon the application or removal of a step voltage has been studied extensively [6–10] to give an insight into the polarization processes. By carrying out the measurements of absorption and short circuit isothermal desorption (discharging) currents at various temperatures, the information such as space charge structure (including the trap distribution of energy and also the volume of the polymer) can be obtained. Such dc step response technique, in which the current response is measured as a function of time after a dc voltage is applied to, or removed from the sample is isothermal analogous of TSDC. It determines the discharging current at constant temperature instead of varying temperatures.

Polystyrene is known to have a good charge storage capability owing to the presence of the phenyl group, which is more electronegative than the methyl group but less than fluorine and hydrogen [11]. The present paper describes the results of simultaneous studies of absorption and discharging current and thermally stimulated discharge current (TSDC) of PS thermoelectret under field and temperature conditions.

Commercial grade polystyrene (PS) used in the present study was supplied by Chemical Agency Bombay. In the present investigation, samples were thermally poled with

*Corresponding Author

field (E_p) of 10–200 kV/cm at various temperatures (T_p) (30–120°C).

The sample preparation, vacuum deposition of electrodes, effective electrode area and geometry, the preconditioning of the samples and the measurement procedure for transient and TSDC in this work were exactly the same as reported in the earlier work [10,12]. The heating rate was 3°C/min.

Current-time characteristics of transient currents in charging and discharging modes are shown in Figures 1–4. The order of current in charging currents is higher

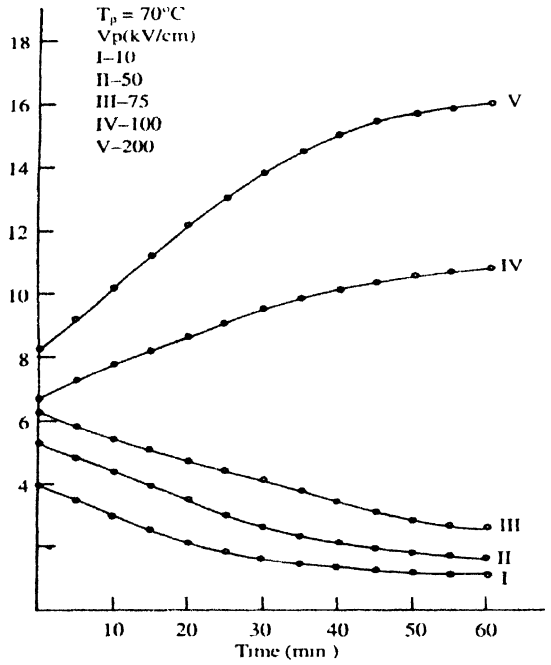

Figure 1. Charging characteristics of PS films with various E_p's at T_p 70°C.

than current observed in discharging mode. Figures 1 and 2 show typical charging currents *vs.* time characteristics for different E_p's (*i.e.* 10, 50, 75, 100 and 200 kV/cm) at 70 and 120°C, respectively. It is evident from these figures that the nature of charging transient currents is approximately similar for all the E_p's at both the temperatures (*i.e.* 70 and 120°C) except for poling fields (10, 50 and 75 kV/cm) at 70°C. The charging currents decreases with time. However, in other cases, the charging currents show an increasing trend and become saturated after about 45 min. It is also clear that with increase in the applied field, the magnitude of charging current increases. Figures 3 and 4 depict the variation of

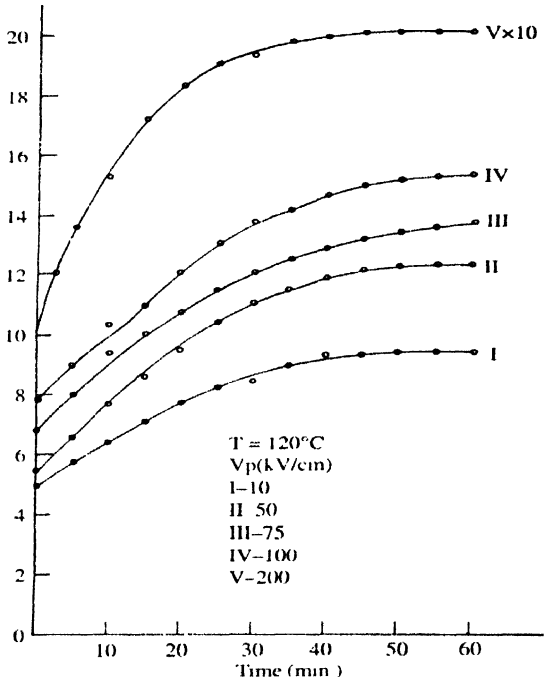

Figure 2. Charging characteristics of PS films with various E_p's at T_p 120°C.

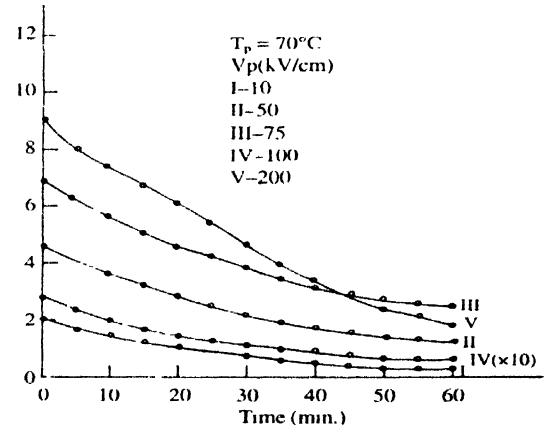

Figure 3. Discharging characteristics of PS films with various E_p's at T_p 70°C.

discharging currents with time. With all the E_p's (10, 50, 75, 100 and 200 kV/cm) at 70 and 120°C, currents decreasing with time. In all the cases, nature of discharging currents is found similar. The magnitude of discharging currents increases with increase in E_p. There appears to be a process of thermal activation over the whole range of temperature. It is found that charging as well as discharging currents have been characterized with logarithmic slopes smaller in magnitude (<1) during the range of short times, and then goes to the longer time

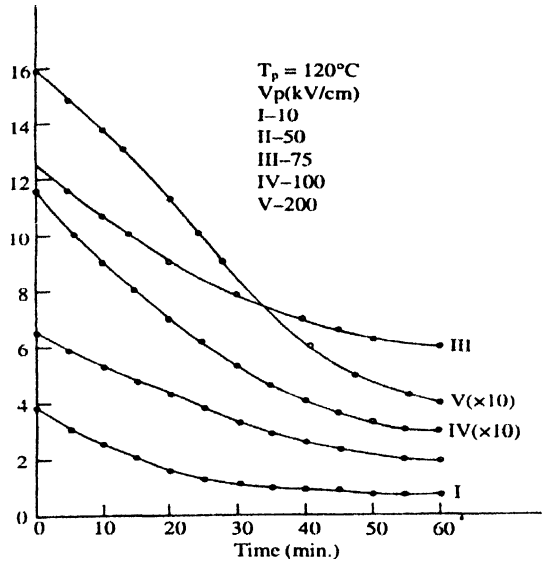

Figure 4. Discharging characteristics of PS films with various E_p's at T_p 120°C.

region (with $n \approx 1.9$) where current tends to approach the saturation or steady state current. The samples were charged with different fields (10–100 kV/cm) at different temperatures. The representative results for samples charged with 50 kV/cm at different T_p's (30, 60, 90 and 110°C). The TSDC thermograms show a single peak located at around 60–85°C (Figure 5). The slight shift in

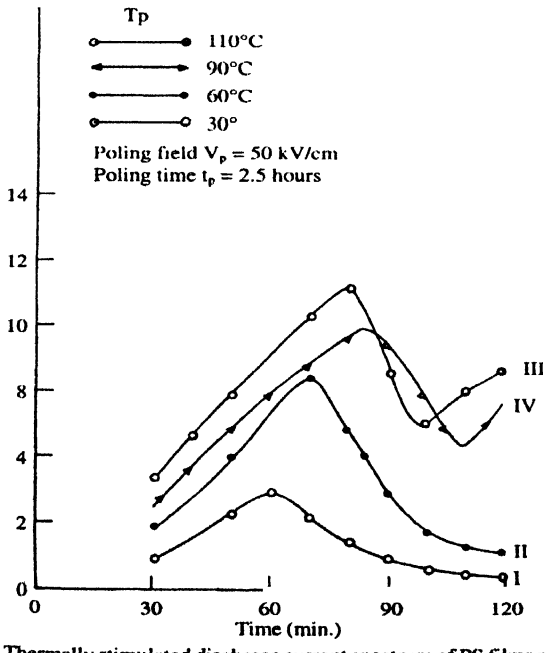

Figure 5. Thermally stimulated discharge current spectrum of PS films poled with 50 kV/cm at different T_p's (*i.e.* 30, 60, 90 and 110°C).

peak observed could be due the slight change in the electret forming conditions and the heating rate. A limited number of measurements were made with samples of 5, 10 and 25 μm thickness over a temperature range with silver, copper, lead and tin electrodes for charging and discharging transients as well as TSDC studies (results not shown) and it is found that there is no evidence of thickness- and electrode-dependence.

A number of mechanism have been proposed [13–15] to explain the current transients observed in homogeneous insulators. The dc step response measurements, in which the current response is measured as a function of time after a dc voltage is applied to, or removed from the sample, are quite similar to TSDC measurements, except for the temperature being constant. However, when the measurements are made at various temperatures, it is possible to collect the dc step data at a specific time and to plot them as a function of temperature [3,4,6]. When an electret is heated to obtain the TSDC, the peak which generally appears near T_g is due to the randomization of the oriented dipoles or due to the release of charge carriers from the traps [16]. Since PS is a non-polar amorphous polymer, dipoles cannot be the main cause of polarization. The phenyl group in PS acts as a strong trapping site for the space charges during electret formation, which are released during TSDC measurement around T_g. For any given electric field, the time-dependence of transient current is found to obey the law of dielectric responses [17,18]. In the present study, the large currents obtained after the application of field, subsided to much smaller steady values after a certain length of time. This is because as the total current is the sum of absorption currents which decays with time and static currents which remains constant. The absorption current reduces to zero when sample is polarized. It is observed that the rate of fall of the absorption current is low for lower E_p than for higher E_p's *i.e.* at higher fields, the current approaches a stable value in relatively shorter time after the field is applied. It means that the polarization time decreases with the increase of E_p, suggesting a dependence of the resistance of the film on the level and duration of applied field. The time-dependent absorption current suggests that the polarization in sample may be due to dipolar orientation and trapping of charge carriers in the bulk, whose injection from the traps will increase with increasing E_p and T_p. The sudden application of voltage causes cloud of carriers *i.e.* a space charge, to

be injected from the contact into the sample. This free charge gives rise to a burst of current. However, one must take into account the effects of trap densities in the sample. The free charge forced into the sample settles into the traps and one observes the decay of current, the rate being determined by the capture cross section of traps for free carriers. The magnitude of charging current is greater than the discharging currents at corresponding temperatures. It appears that charge involved in the charging period is greater than the discharge period. The possible reason for this difference may be that the initial transients occur with empty traps and currents will be as large as allowed by the injecting barriers. As the traps become filled, the current reduces to the space charge limited currents with traps. In the discharging period, on the other hand, the trapped carriers will be discharged towards both electrodes showing a smaller current in the external circuit. The Curie-Von Schweidler law was not found to be obeyed for a longer period of time and the latter becomes progressively shorter (*i.e.* more and more limited period of time) with the increase in temperature [19]. The decrease in free volume lowers the mobility of chain segments and also charge carriers. The decrease in mobility may be expected to reduce the conductivity. At higher E_p's, a change in mobility may take place faster than at lower E_p's and also recombination of charge carriers may be more. The above processes may be responsible to make the observed current in the present case to approach a stable value in relatively shorter periods under higher fields [20]. In the present case, the charging currents for samples poled at 70°C (with E_p's 100 and 200 kV/cm) and 120°C (with all E_p's) was found to increase monotonically with time and tend to saturate. Under higher E_p and T_p, the electrons and holes are likely to drift through the sample bulk and accumulate at the metal-polymer interfaces, because the contacts are supposed to be blocking to transport. The hetero space charge formed at the metal-polymer interface will result in a very intense field over the interface. Such a high field may cause the continuous increase in current with time. In the present case the current has been observed to be activated thermally. Tunneling can be unequivocally eliminated as a possible mechanism in the present case, since the currents are strongly temperature-dependent. Furthermore, the electrode polarization mechanism seems not to be operative in the present case. The electrode polarization predicts the strong dependence of the electrode material on the decay of the transient currents. Moreover, uniform and electrode polarization requires the charging and discharging currents at a particular instant to vary linearly with charging field. The charging and discharging at various times after the application or termination of field are found to follow the power law-dependence on field. The observed divergence from Ohms law at high fields and the thermal activation of discharge current at various prescribed times, indicate the space charge formation. The various facts including non-polar structure of PS, power law-dependence of current on field observed values of 'n' and thermal activation of current over temperature range as observed in present case, indicate that the space charge due to accumulation of charge carriers near the electrodes and trapping in the bulk may be supposed to account for the observed currents. The decay of current in the long time region for different samples, indicates the existence of energetically distributed localized trap levels in the sample. It seems that at shorter times, only the shallow traps get emptied contributing to stronger current. However, at longer times, deeper traps with long detrapping times release their charges and the current decays at longer times. Discharging current, measured at various prescribed times, *vs.* temperature plots (results not shown), are characterized by a peak located at 75°C, however, no shift is observed in the peak temperature with time of observation. The peak is broad and probably it contains several minor processes, one of which may be associated with the T_g of the polymer and the other may be due thermal release of trapped carriers. The broadness of the peak may be explained by assuming a distributed or multiple dielectric relaxations, which may be due to distribution in activation energy when the rotation of the dipoles does not proceed in the same environment. Alternatively, it may be due to distribution in relaxation time, when the rotational masses of dipoles are not equal. The broadness of the peak in the present case is, however, most likely to be distribution in relaxation time, because the peak is occurring near T_g of the polymer.

The TSDC thermogram shows a peak centered at 60–85°C. The value of activation energy (E) has been found to be 0.38 eV. This peak may be either due to dipolar origin or migration of charge carriers through microscopic distance with trapping. In PS, the possibility of permanent dipole alignment is ruled out. However, the polarization process may be assumed to be due to the local movement of molecular chains causing the release of trapped charge.

The origin of space charge in PS can possibly be due to the injection of charge carriers from electrode, the charge trapped in the amorphous crystalline interface of the polymer or the microscopic ion displacement. The phenyl group in PS acts as a strong trapping site for the space charges during TSD measurement.

The equivalent time (t_e) at the TSDC peak temperature T_m was evaluated from the relation [21]

$$t_e(T_m) = hK\frac{T_m^2}{E}, \qquad (1)$$

where, h is the reciprocal heating rate and K is the Boltzman's constant. Using the values of T_m and E for the observed peak, $t_e(T_m)$ was found to be 3.88 min. The TSDC peak, thus can reasonably be compared with the isochronal I_d *vs.* T plot at a constant equivalent time of 4.0 min. The E values obtained from isochronals were found to be 0.42 eV and agree well with the activation energy of 0.38 eV obtained from the TSDC peak. The value of E is small compared with the 1 eV typically required for the measurement of ions, hence suggesting the simultaneous action of dipolar orientation (if any) along with the migration of electrons/holes released from the valence band through microscopic distances with subsequent trapping.

The present study clearly exhibits that the TSDC peak can be investigated by isothermal step response measurements. The decay of charge/discharge currents can best be described in terms of a space charge mechanism and hence, the observed TSDC peak can at least partly be attributed to the dissipation of space charges during heating in a short circuit.

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